

CLAIMS

1. An organic positive coefficient thermistor comprising: a heat-curable polymer matrix, a low molecular weight organic compound, and electrically conductive particles having spike-shaped projections.

5. The organic positive coefficient thermistor according to any of claims 1 to 4, wherein the heat-curable polymer matrix is either an epoxy resin, unsaturated polyester resin, polyimide, polyurethane, phenolic resin or silicone resin.

[0014] [Means for Solving the Problems] The above-mentioned object is achieved by the present invention as described below.

(1) An organic positive coefficient thermistor comprising: a heat-curable polymer matrix, a low molecular weight organic compound and electrically conductive particles having spike-shaped projections.

(5) The organic positive coefficient thermistor described in any of (1) to (4) above, wherein the heat-curable polymer matrix is either an epoxy resin, unsaturated polyester resin, polyimide, polyurethane, phenolic resin or silicone resin.

[0017] Moreover, in the present invention, a heat-curable polymer is used for the matrix. In the present invention, although a large change in resistance is obtained during operation by utilizing a large

volumetric expansion accompanying melting of a low molecular weight organic compound, in the case of a composition consisting of a low molecular weight organic compound and electrically conductive particles alone, the shape of the device is not maintained during operation due to the low melt viscosity of the low molecular weight organic compound. Consequently, in order to prevent flow caused by melting of the low molecular weight organic compound during operation, deformation of the device and the like, it is necessary to disperse the low molecular weight organic compound and electrically conductive particles in a matrix polymer. In the case of using a heat-curable polymer for the matrix polymer, there are problems particularly with respect to high-temperature stability due to the polymer melting at temperatures equal to above the melting point. In the present invention, since a heat-curable polymer is used for the polymer matrix, and the low molecular weight organic compound and electrically conductive particles are dispersed in a non-dissolving, non-melting, three-dimensional mesh-like matrix, characteristics stability is improved considerably and low room temperature resistance and large changes in resistance during operation are stably maintained over a long period of time in comparison with the use of thermoplastic polymers.

[0020] Although there are no particular limitations on the heat-curable polymer matrix, epoxy resin, unsaturated polyester resin, polyimide, polyurethane, phenolic resin or silicone resin is used preferably.

[0021] Epoxy resins are resins in which an oligomer (having a molecular weight of several hundred to about ten thousand) having a reactive epoxy group on the terminal thereof is cured (crosslinked) with various curing agents, and are classified into glycidyl ether types as typically represented by bisphenol A, glycidyl ester types, glycidyl amine types and alicyclic types. Multifunctional epoxy resins having three or more functional groups can also be used depending on the application. In the present invention, a glycidyl ether type, and particularly bisphenol A, is used preferably. The epoxy equivalent of the epoxy resin used is preferably about 100 to 500. Curing agents are classified into polyaddition types, solvent types and condensation types according to the reaction mechanism. Polyaddition types are such that the curing agent itself is added to an epoxy group or hydroxyl group, examples of which include polyamines, acid anhydrides, polyphenols, polymercaptans and isocyanates. Solvent types catalyze polymerization among epoxy groups, examples of which include tertiary amines and imidazoles. Condensation types induce curing by condensing with a hydroxyl group, examples of which include phenolic resins and melamine resins. In the present invention, a polyaddition type, and particularly a polyamine or acid anhydride, is preferably used for the curing agent of bisphenol A-type epoxy resin. The curing conditions may be suitably determined.

[0022] These types of epoxy resins and curing agents are available commercially, examples of which include Epicoat (resin), Epicure and Epomate (curing agent) manufactured by Yuka-Shell Epoxy Co., Ltd., and Araldite manufactured by Nihon Ciba-Geigy K.K.

[0033] Although the heat-curable resin used can be suitably selected according to the desired performance and application, epoxy resin or unsaturated polyester resin is used preferably. In addition, two or more types may be mutually reacted to form a polymer.

[0039] One type or two or more types of low molecular weight organic compounds can be selected and used according to the operating temperature and the like for the low molecular weight organic compound.

[0040] The weight of the low molecular weight organic compound is preferably 0.2 to 4 times, and particularly preferably 0.2 to 2.5 times, the total weight of the heat-curable polymer matrix (including curing agent and the like). If this mixing ratio is too small and the amount of low molecular weight organic compound is too low, it becomes difficult to obtain an adequate resistance change ratio. Conversely, if the mixing ratio is too large and the amount of low molecular weight organic compound is too high, in addition to the device becoming excessively deformed when melting the low molecular weight organic compound, it also becomes difficult to mix the electrically conductive particles.

[0041] The electrically conductive particles having spike-shaped projections used in the present invention are formed from primary particles each having individual sharp projections, and a plurality of conical, spike-shaped projections having a height of $1/3$ to $1/50$ particle diameter are present on a single particle (normally 100 to 500

projections). These particles are preferably made of metal, and particularly preferably nickel and the like.

[0042] Although these electrically conductive particles may be in the form of a powder in which each particle is present separately, about 5 10 to 1000 primary particles are preferably connected in the manner of a chain to form secondary particles. Primary particles may also be present in a portion of these chain-like secondary particles. An example of the former is spherical nickel powder having spike-shaped projections that is commercially available under the product name 10 Type 123 Nickel Powder INCO (Inco TNC Ltd.), has a mean particle diameter of about 3 to 7 μm , has an apparent density of about 1.8 to 2.7 g/cm^3 , and has a specific surface area of about 0.34 to 0.44 m^2/g .

[0043] In addition, an example of the preferably used latter particles is a filamentous nickel powder that is commercially available under 15 the product names INCO Type 210, 255, 270 and 287 Nickel Powder (Inco TNC Ltd.), of which INCO Types 255 and 287 are preferable. The mean particle diameter of primary particles thereof is preferably 0.1 μm or more and more preferably about 0.5 to 4.0 μm . Among these, a primary particle mean particle diameter of 1.0 to 4.0 μm is 20 most preferable, and particles having a mean particle diameter of 0.1 to less than 1.0 μm may be mixed therein up to 50% by weight. In addition, the apparent density is about 0.3 to 1.0 g/cm^3 , and the specific surface area is about 0.4 to 2.5 m^2/g .

25 [0061] [Examples] The following provides a detailed explanation of the present invention by indicating examples and comparative

examples thereof.

<Example 1> A heat-curable polymer matrix in the form of bisphenol A epoxy resin (Yuka-Shell Epoxy Co., Ltd., product name: Epicoat 801), a denatured-amine curing agent (Yuka-Shell Epoxy Co., Ltd., product name: Epomate B002), a low molecular weight organic compound in the form of paraffin wax (Nippon Seiro Co., Ltd., product name: HNP-10, melting point: 75°C), and electrically conductive particles in the form of filamentous nickel powder (INCO TNC Ltd., product name: Type 255 Nickel Powder) were used. The mean particle diameter of the electrically conductive particles is 2.2 to 2.8 μm , the apparent density is 0.5 to 0.65 g/cm^3 and the specific surface area is 0.68 m^2/g .

[0062] 20 g of bisphenol A epoxy resin, 10 g of denatured amine curing agent, 15 g of paraffin wax (0.5 times the total weight of the epoxy resin and curing agent), 180 g of nickel powder (4 times the total weight of the organic components) and 20 ml of toluene were mixed for about 10 minutes with a centrifugal disperser. After coating the resulting paint-like mixture on one side of a nickel foil electrode having a thickness of 30 μm , the mixture was sandwiched in between with another nickel foil electrode, placed between brass plates and adjusted to a total thickness of 1 mm with spacers followed by heat-curing for 3 hours at 80°C while pressed together with a hot press. The sheet-like cured product in which the electrodes were hot-pressed was punched out into the shape of a disk having a diameter of 1 cm to obtain an organic positive coefficient thermistor device. A schematic cross-sectional view of this thermistor device is

shown in FIG. 1. As shown in FIG. 1, this thermistor device has a thermistor element 12, in the form of a sheet-like cured product containing a low molecular weight organic compound, a polymer matrix and electrically conductive particles, sandwiched between electrodes 11 formed from nickel foil.

[0063] This element was then heated from room temperature (25°C) to 120°C at the rate of 2°C/minute in a constant temperature chamber and then cooled followed by measuring the resistance value using the four electrode method at a predetermined temperature to obtain a temperature-resistance curve. Those results are shown in FIG. 2.

[0064] The initial room temperature resistance (25°C) was $8.2 \times 10^{-3} \Omega$ ($6.4 \times 10^{-2} \Omega \cdot \text{cm}$), the resistance value increased rapidly in the vicinity of the melting point of the wax of 75°C, and the resistance change ratio was 10 digits or more. There were no decreases in resistance (negative temperature coefficient (NTC) phenomena) observed even after increasing the resistance and continuing to heat to 120°C. In addition, the temperature- resistance curve during cooling did not vary greatly from that during heating, and hysteresis was sufficiently small.